NANO VISION
An International Open Free Access, Peer Reviewed Research Journal
www.nano-journal.org

ISSN 2231-2579 (Print)
ISSN 2319-7633 (Online)
Abbr: Nano Vision.
2013, Vol.3(3): Pg.209-214

Structural and Optical Characterization of Nanoscale CdO:Mn Thin films prepared by Chemical Spray Pyrolysis Technique

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Presented in First National Conference on Thin Film Science and Nano Technology (FIRST-NCTFSANT-2013) September 2-3, 2013, Rajah Serfoji Govt. College, Thanjavur, T.N.(India).

ABSTRACT

A great deal of research efforts was directed towards investigation of the physical properties of thin film to improve the quality and performance of the device and for finding new applications. In this study, undoped cadmium oxide (CdO) and manganese doped cadmium oxide (CdO:Mn) films were deposited onto glass substrates by home built spray pyrolysis technique at 250C temperature. The structure of the undoped and manganese doped films were studied by X-ray diffraction have polycrystalline structure with (111) preferential orientation. X-ray peak line was studied to estimate grain size, strain and other orientations. The transmittance in visible and NIR region with direct optical band gap were estimated for undoped CdO and manganese doped CdO. The results were analyzed for three different concentrations of Mn doped CdO films and are reported.

Keywords: Undoped cadmium oxide, spray pyrolysis technique.

INTRODUCTION

The transparent conducting oxide thin films such as zinc Oxide (ZnO), Indium tin oxide (ITO), tin oxide (SnO_2) and cadmium oxide (CdO) are extensively used in semiconductor optoelectronic applications[1-3]. CdO is an n-type semiconductor with a rock-salt crystal structure (FCC) and posses direct band gap between (2.3 and 2.5) eV[4]. Its high electrical conductivity (even without doping) and high optical transmittance in the visible region of solar spectrum[5] which has found extensive applications in solar cells[6], low

emissive window optical communications, flat panel display, photo transistors, photo diodes, transparent electrodes and gas sensors[7-11]. In this work, our aim is to produce a CdO based material with better characteristics (optical, structural) and stability, than CdO by Mn incorporation for photo voltaic application.

MATERIALS AND METHODS

Manganese doped cadmium oxide thin film were deposited on the glass substrate from aqueous solution of cadmium acetate with a concentration of 0.05M dissolved in 25ml of double distilled water. For doping with manganese different concentration 0.0001, 0.0002 and 0.0003 M of manganese acetate was dissolved in distilled water of 25 ml and both are mixed together to form a 50ml precursor solution. Prior to spraying the precursor solution on to glass substrates, they were cleaned by soap solution and acetone and dried. The precursor solution is deposited by spray method onto the preheated glass substrates kept at temperature 250ºC. In order maintain a content temperature of 250ºC during spray deposition process the hot plate of electric furnace is controlled by temperature thermo controller. The nozzle to substrate distance was approximately 30cm and nozzle is kept at an angle of 45º and the successive spray time was 5 seconds for spraying and 15 seconds left for avoiding excessive cooling of substrate. The films were prepared with 50 ml of solution which was sprayed by successive spray method for 30-35 minutes at constant flow rate 3 ml/min.via compressed carrier gas. Compressed carrier gas which is kept at a pressure of 2 $kgcm^{-2}$ of gas released from air compressor through air filter and regulator to get a fine mist of spray. The Mn doped CdO were prepared with different concentration which is shown in table 1.

Table 1. Prepared CdO : Mn Concentration

Material	Cadmium acetate in ml	Manganese Acetate tetra hydrate in ml	Volume of solution in ml
Undoped CdO	50 (0.05M)	Nil	50
CdO : Mn	25 (0.05M)	25 (0.0001M)	50
CdO : Mn	25 (0.05M)	25 (0.0002M)	50
CdO : Mn	25 (0.05M)	25 (0.0003M)	50

The structural, optical and morphology studies were investigated using X-ray diffractometer, optical spectrometer and scanning electron microscope (SEM) and reported.

RESULTS AND DISCUSSION

The structural analysis was carried out by recording X-ray diffraction (XRD) spectrum using X-ray diffractometer (PANalytical X'Pert) recorded in the 2θ range from 10 to 90 with step size of 0.02° using cu-kα radiation (λ=1.54056Å). The XRD spectra of undoped and Mn (0.0001, 0.0002 and 0.0003 M) doped are shown in figure 1. The obtained XRD pattern is compared with JCPDS card [75-1529] indicating polycrystalline nature with face centered cubic crystal structure, the planes

are indexed as (111),(200), (220), (311) and (222) with respect standard card XRD lines shows broadened in their shape when compared with standard JCPDS line. The preferential growth is along (111) plane is observed for undoped CdO films and manganese doped CdO films. The preferential orientation is changed from (111) plane to (200) for the higher concentration to lower concentration of manganese. The grain size was calculated using Scherrer formula[12] for preferential planes. The grain size increased rapidly upon increasing the Mn concentration. The grain size of the undoped film was found to be 25 nm which increased to in the range of 31-40 nm for 0.0001 – 0.0003 of Mn. The peak angle values and grain size obtained for both undoped and doped CdO films are given in table 2. Decrease in grain size increases in microstrain which indicates peak movement without change in the shape of the peak.

Table 2. XRD obtained undoped and Mn doped CdO

Mn Doping concentration	2θ	Grain size	Strain	FWHM
0.0001M	33.083	31.42	0.001816	0.50
0.0002M	33.08	40.29	0.001416	0.39
0.0003 M	33.09	33.43	0.001706	0.47
Undoped CdO	32.95	25.46	0.002261	0.61

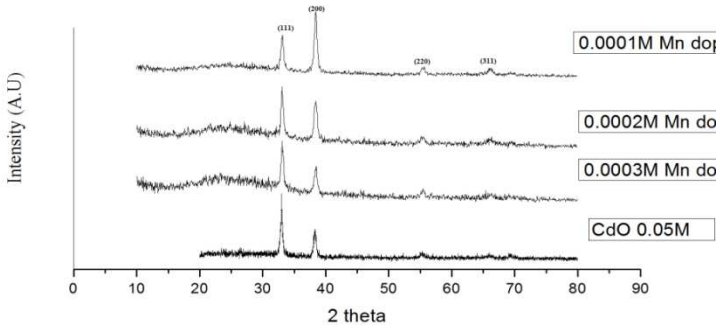

Figure (1): X-ray diffraction pattern of CdO : Mn thin film prepared various concentration at (250Co).

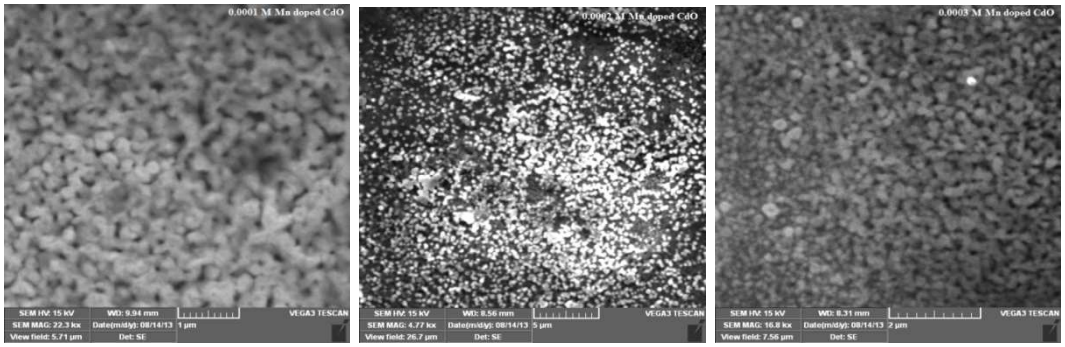

Figure 2: SEM images of CdO:Mn thin films for various concentration

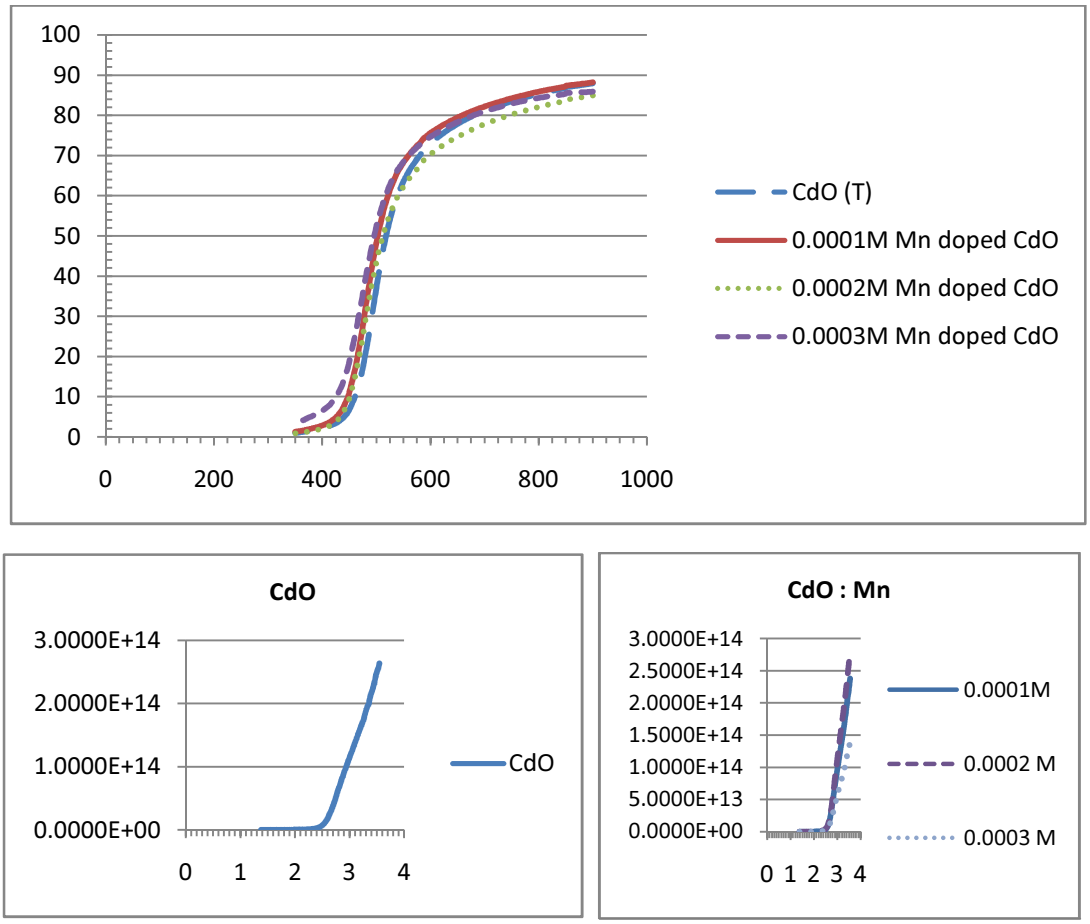

Figure 3: UV-VIS spectra of transmission and bandgap plots of CdO:Mn thin films for various concentration.

Morphological Studies

Surface Morphology of the films was investigated by using TESCAN Vega scanning electron microscope with an accelerating potential of 15 kv. The film has porous with grains composed a smaller crystallites. It shows the Mn:CdO deposited n glass substrate was grown as spherical shape grains like morphology. Each grain can be indexed to have cubic crystalline.

Optical characterization

Figure shows optical absorbance and transmittance of Mn:CdO film prepared at optimized condition. It shows smooth increase in transmission above 600 nm. Figure reveals high transparence in visible and NIR regions is in good agreement with the reported results for CdO thin film[14]. This smooth increase is due to crystalline nature of prepared film. The maximum transmission

found to be 89% at 900 nm. The absorption coefficient α is calculated from Lamberts law

$\alpha = 2.303\, A/t$

Where t is optical absorbance and t is the thickness of the film obtained loss of weight method (Akyuz *et al*. 2011).

The transmission of the film is more than 87% and the presence of Mn does not decrease the transmission. The doping of the Mn results in the shift of edge towards lower wavelength for increase in manganese content. From plot between $(\alpha h\nu)^2$ and hν as shown in figure direct allowed band gap were determined.

The increase in the Mn concentration results in sharp increase of optical band gap with Mn doping the shift in the absorption is clearly seen in figure. The graph is extraploted to give Eg value is found to be 2.5 – 2.6 ev and agree with the literature report[15]. The Eg. value can be calculated using the fundamental absorption, which corresponds to electron excitation from the valance band to conduction band. Eg is usually obtained by extrapolations of the linear portion of the plots of $(\alpha h\nu)^2$ vs. hν, as shown in Figure 3.

CONCLUSIONS

Mn doped CdO films were coated on glass substrates at 250ºC by spray pyrolysis technique. X-ray diffraction, Transmission spectra, absorption spectra and bandgap were investigated. XRD pattern confirms CdO phase with preferential orientation along (111). The grain size increased rapidly upon increasing the Mn concentration. The grain size of the undoped film was found to be 25 nm which increased to 40 nm for 0.0002 of Mn. Surface morphology studies shows that the Mn:CdO deposited glass substrate was grown as spherical shape grains. Films have good transmission in UV/Vis region. The transmission of the film is more than 87% and the presence of Mn does not decrease the transmission. The graph is extraploted to give Eg value is found to be 2.5 – 2.6 ev. Finally, it has been concluded that Mn doped CdO films have improved roperties and are good candidates for photovoltaic application.

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